# SYNTHESIS AND MASS SPECTRA OF CYCLOPROPENE AND CYCLOPROPENONE

A THESIS

Presented to

The Faculty of the Graduate Division

by

Marshall Ashworth Bell

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemical Engineering

Georgia Institute of Technology

May, 1968

SYNTHESIS AND MASS SPECTRA OF CYCLOPROPENE AND CYCLOPROPENONE

Approved:

Chairman

Date approved by Chairman: May 16, 1968

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# ACKNOWLEDGMENTS

I am grateful to Dr. H. A. McGee, Jr. for his suggestions, assistance, and encouragement during my graduate studies. The help and assistance of Dr. C. L. Liotta and Dr. W. T. Ziegler who served on my reading committee is appreciated, as was the help of my colleagues, Mr. R. J. Holt and Dr. A. F. Stalder of the Cryochemistry Laboratory. Mr. Holt worked full time with me during the last few months needed to complete this work and all TOF mass spectrometric data that are reported herein were obtained by him.

I wish to thank the National Aeronautics and Space Administration for Grant NsG-337 which provided for the materials used in this work as well as for a research assistantship for myself.

Appreciation is due Mr. Ping H. Li, Mr. Joe Floyd, and Mr. Phil Torline for their help in analyzing samples and to Mr. D. E. Lillie for his expert glassblowing. I am especially grateful to Dr. J. A. Knight of Georgia Tech and Mr. Gordon Ryan of Columbia University for their helpful advice during the conduct of this work. Finally, I wish to thank Miss Ginga Jacobson for typing this thesis.

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# SUMMARY

Production of cyclopropene and cyclopropenone has been successfully accomplished using the most recent synthesis techniques available.

Cyclopropene was prepared by the reaction of allyl chloride and sodium amide in a mineral oil suspension. The evolved gaseous products were passed through a sulfuric acid bath, then trapped in a receiver immersed in liquid nitrogen ($77^{\circ}$ K). Because of its highly unstable character, cyclopropene was kept at liquid nitrogen temperature until time for its analysis or its subsequent utilization.

Cyclopropenone was prepared by the reaction of tri-n-butyltin hydride with tetrachlorocyclopropene in mineral oil, followed by distillation of the product to yield a volatile mixture of dichlorocyclopropenes which was hydrolyzed to form the final product.

Because neither tetrachlorocyclopropene nor tri-n-butyltin hydride are commercially available, it was first necessary to prepare these compounds.

The first step in the synthesis of tetrachlorocyclopropene involved the reaction of trichloroethylene with sodium trichloroacetate in dimethoxyethane as a solvent. The oil produced in this step was distilled to yield pentachlorocyclopropane, which was then dehydrohalogenated with potassium hydroxide to give tetrachlorocyclopropene.

The synthesis of tri-n-butyltin hydride was accomplished by the reaction of lithium aluminum hydride with tri-n-butyltin chloride in ether solution. The ether solution of the product was washed and distilled to

give tri-n-butyltin hydride product.

Cyclopropene and cyclopropenone have been produced in usable quantities and stored for concurrent and future studies of their molecular energetics. The basic steps in the preparation of these two compounds followed those given in the literature, but a number of changes of modifications were found to be desirable for convenience of technique or for optimum yield. This study should serve as a manual for preparing cyclopropene and cyclopropenone for future research.

# CHAPTER I

# INTRODUCTION

## General Problem

Much work is currently being conducted in chemical kinetics on the elucidation of the mechanisms by which chemical reactions occur. In some cases the detection of compounds intermediate between reactants and products can give evidence as to the steps involved in the mechanism.

One of the newest and most successful tools used in the study of the energetics of unstable compounds is the cryogenic mass spectrometer developed in the Cryochemistry Laboratory of the Georgia Institute of Technology. The development of the cryogenic mass spectrometer and some of its past applications are fully discussed in theses from this laboratory by Martin[1], Malone[2], and Bivens[3].

## Purpose of Research

The purpose of this work is to produce, in usable quantities, cyclopropene and cyclopropenone, two recently prepared highly strained and unstable small ring hydrocarbons. These compounds are to be used in concurrent and future studies of the energetics and stability of several reaction intermediates when maintained at cryogenic temperatures.

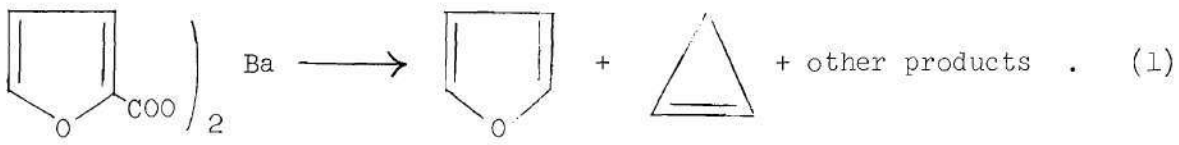
The most successful and most easily manageable syntheses were chosen as models to use in the preparation of cyclopropene and cyclopropenone. The work of Closs and Krantz[4] was selected as being the most practical in preparing cyclopropene, while the very recent work of Breslow

and Ryan[5] served as a guide for the preparation of cyclopropenone.

## Past Work on Cyclopropene

As a result of the bond strain that is present in cyclopropene and cyclopropene derivatives, these compounds lend themselves nicely to a study of the effects of ring substituents on the properties of carbon-carbon and carbon-hydrogen bonds. The effects of substituents are exaggerated in the unsaturated three-membered ring, and for this reason a considerable amount of attention has been given to the cyclopropenes.

In 1897 Freundler[6,7] reported the synthesis of cyclopropene by the pyrolysis of barium furoate according to the reaction



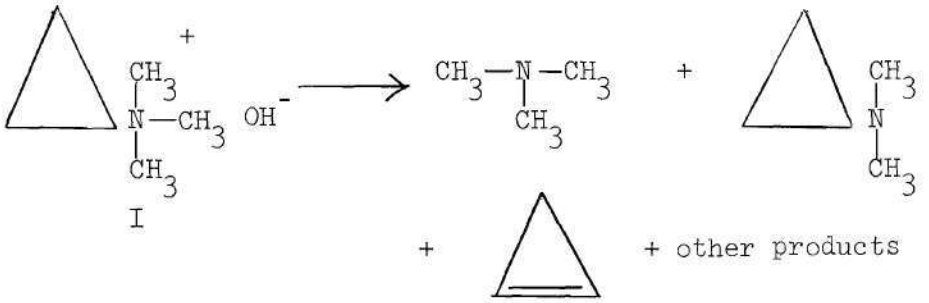

(1)

This gaseous substance with an alliaceous odor was reported to be slightly soluble in water, gave no precipitate with either ammoniacal cuprous chloride or silver nitrate, but did yield a precipitate from alcoholic solutions of mecuric chloride. The gas reacted with bromine to give a small quantity of dibromide as well as one or more tetrabromides. The formation of the tetrabromide $CHBr_2CH_2CHBr_2$ indicated that the unsaturated hydrocarbon synthesized was cyclopropene. Although furan was the principle product formed, the gas was obtained in 5 to 6 percent yields[8].

A later study of the method confirmed the formation of furan and other products, but indicated no appreciable yields of cyclopropene[9]. Possibly the temperature necessary for this dry distillation procedure caused the transformation of any cyclopropene formed into a polymer, or

into methylacetylene, or into some other substance. Methylacetylene was identified as a reaction product but was found only in small amounts.

The first confirmed report of the synthesis of cyclopropene was that of Dem'yanov and Doyarenko[10,11], who obtained the hydrocarbon by the thermal decomposition of trimethylcyclopropylammonium hydroxide on platinized clay at approximately 300° according to the reaction

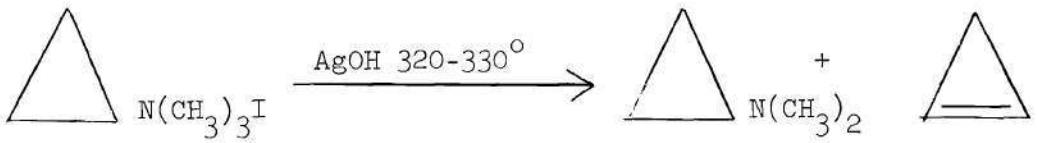


(2)

Trimethylamine and dimethylcyclopropylamine were also obtained. The reaction was carried out in an atmosphere of carbon dioxide and away from direct light in order to prevent extensive oxidation and polymerization of the cyclopropene product. The cyclic compound reacted with bromine to give two bromides, a dibromide, and a tetrabromide. Although the tetrabromide, $CHBr_2CH_2CHBr_2$, was stated to be reduced quantitatively to cyclopropene by zinc dust and ethyl alcohol, this reduction was not confirmed[12]. The presence of a small amount of $CH_3CBr_2CHBr_2$ indicated that methylacetylene was also formed from the decomposition of the quaternary base. Further experiments[13] showed that an increase in the temperature for the decomposition resulted in an increase in the amount of methylacetylene formed and a decrease in the amount of cyclopropene.

The Russian work was confirmed in an extensive investigation[12] of the reaction conditions necessary for a preparative scale operation. An

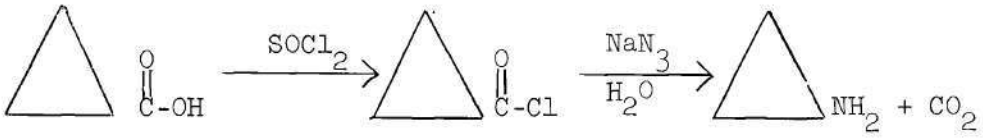
approximately 4.7 percent overall yield of cyclopropene was obtained at the optimum temperature of 320-330°. The pure compound was obtained by fractional distillation of the hydrocarbons formed from the pyrolysis of the trimethylcyclopropylammonium iodide. Each step in the synthesis was studied from a preparative point of view. Dimethylcyclopropylamine and methylacetylene were also obtained. Whereas the ratio of hydrocarbons to amines seemed to be affected by the condition of the catalyst, the ratio of cyclopropene to methylacetylene depended mainly on the temperature.




(3)

+ other products .

This procedure was modified[14] slightly by using the Schmidt reaction for the conversion of cyclopropanecarboxylic acid to cyclopropylamine as given by the reaction



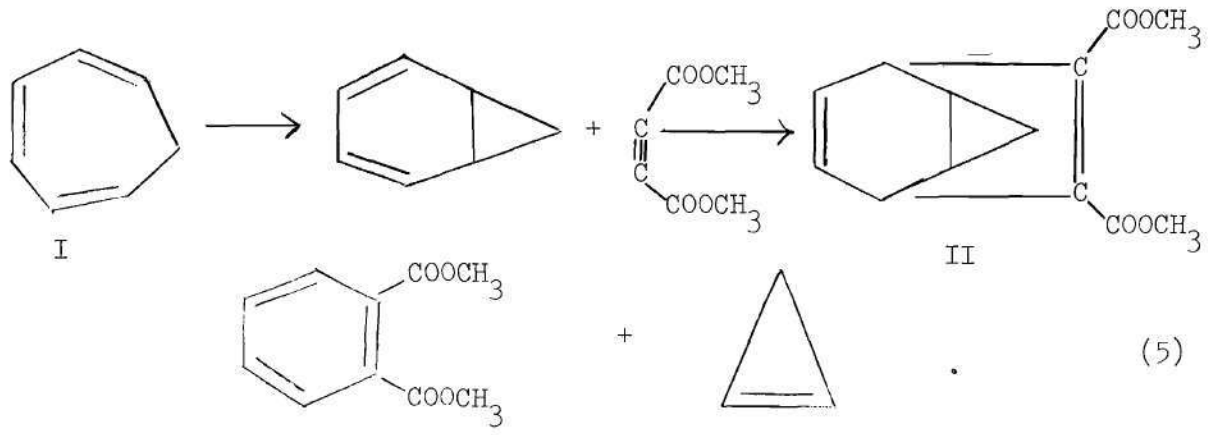

(4)

The cyclopropene was purified by vapor phase chromatography with the removal from the gaseous mixture of such impurities as ethylene, carbon dioxide, methylacetylene, and dimethyl ether.

A deuterated sample of cyclopropene has been prepared by equilibrating the cyclopropyltrimethylammonium hydroxide with deuterium oxide before pyrolysis[14]. Mass spectrometric analysis showed that the cyclopropene sample

obtained had 40 percent cyclopropene-$d_2$, 40 percent cyclopropene-$d_1$, and 20 percent cyclopropene-$d_0$[15]. An analysis of the nmr spectrum of the dibromide derivative indicated that 80 percent of the deuterium was in the vinyl position, thereby supporting the evidence[16] that vinyl hydrogen in a cyclopropene derivative is moderately acidic[14].

A gas believed to be cyclopropene along with a phthalic acid ester was cleaved from an adduct (II in Equation (5)) formed by the reaction of cycloheptatriene (I in Equation (5)) and dimethyl acetylenedicarboxylate[17,18]. In a further investigation[14], quantitative yields of the phthalate were obtained but only 1 percent of cyclopropene, as the remainder, was found in the form of a cyclopropene polymer.




(5)

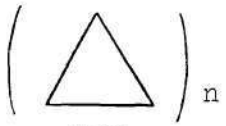
## Chemical Reactions of Cyclopropene

The properties of cyclopropene are of interest to investigators studying the effect of ring strain on bond hybridization and reactivity. A number of cyclopropene reactions were investigated with special interest in the effect of bond angle deformation on the reactions.

The thermal isomerization of cyclopropene to methylacetylene was

found to proceed slowly at 325° but fairly rapidly at 425°. Cyclopropene was not obtained in detectable quantities when methylacetylene was treated similarly[14].

The major portion of cyclopropene was polymerized upon attempted fractional distillation at -36°, its boiling point at atmospheric pressure. Polymerization occurred readily at room temperature and was assumed to be a free-radical chain reaction. The nmr spectrum indicated the structure of the polymer to be that of a polycyclopropane (III)[14].

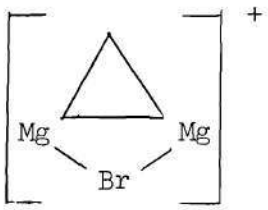


III

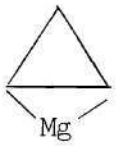
Although cyclopropene could not be stored even at dry-ice-acetone temperature (-78°), 1,2-dimethylcyclopropene may be kept in a refrigerator without polymerization[20].

Cyclopropene was quantitatively removed from a mixture with nitrogen when the mixture was passed through an aqueous or ammoniacal silver nitrate solution[21,14]. The formation of the silver complex possibly imparted some $sp^3$ character to the double bond and was thus related to the relief of angle strain by the lengthening of the double bond.

Cyclopropene reacted with iodine in carbon tetrachloride solution to form 1,2-diiodocyclopropane, a very stable compound which did not react with iodide ion or with zinc dust to reform cyclopropene[14]. Cyclopropene also readily added bromine to form a dibromide with the trans configuration. The dibromide formed a di-Grignard reagent with the probable structure formulated as

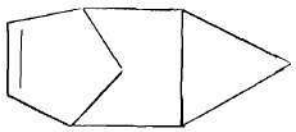



where the magnesium atoms and the bromine are associated in a way similar to an ion-triplet, or where there may be some covalent character to the association. An alternate structure for the Grignard reagent was suggested as



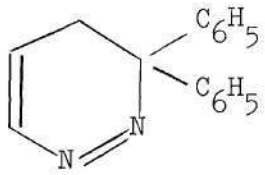

[22,14]. Other preliminary experiments[23] indicated that cyclopropene may not react with Grignard reagents under conditions where cyclopentadiene is converted to cyclopentadienylmagnesium compounds.

Cyclopropene behaved as a dienophile and underwent Diels-Alder reaction when it was passed into a cold solution of cyclopentadiene in methylene chloride. The expected adduct



was obtained in 97 percent yield. Only a 37 percent yield was obtained with the less reactive butadiene[14,22].

Diphenyldiazomethane reacted with cyclopropene, even in the presence of copper powder, to form a 1:1 addition compound with the probable structure



A six-membered unsaturated ring was obtained in a similar fashion by the reaction of cyclopropene with diazoacetic ester, with the reaction proceeding rapidly even at temperatures as low as -40°[14].

Although the derivatives of cyclopropene undergo many reactions, they will not be discussed in this work. Carter and Frampton[24] give a very good summary of these reactions along with physical and physicochemical properties of cyclopropene and its derivatives.

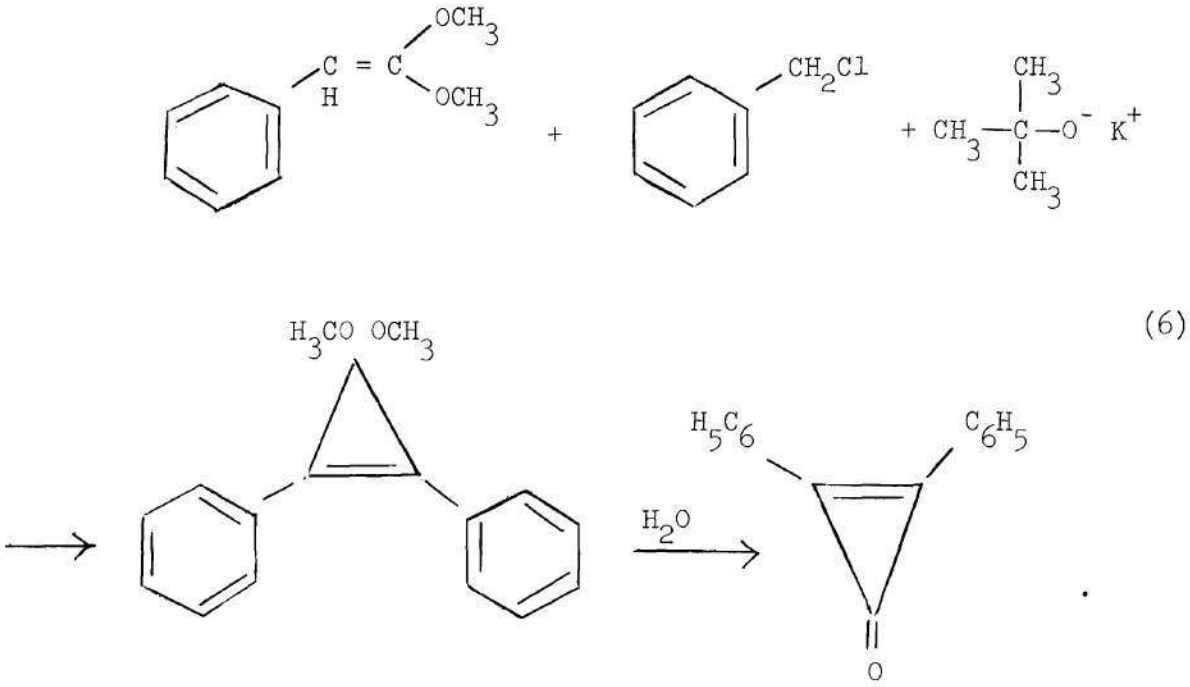
## Previous Work on Cyclopropenone

All of the major work on cyclopropenone and its derivatives has been conducted by Breslow and his associates.

In 1959 Breslow stated that, up to that time no stable compound was known containing a carbonyl group in a three-membered ring. He considered that the reaction between a carbene and a ketene acetal to furnish a cyclopropene ketal[26] could be adapted for this purpose. The reaction of phenyl ketene dimethyl acetal[27] with benzyl chloride and potassium t-butoxide was selected, and is shown on the following page.

The expected product was the dimethyl ketal of diphenylcyclopropenone, but with aqueous processing this hydrolyzed forming only diphenylcyclopropenone itself; melting point: 121°.

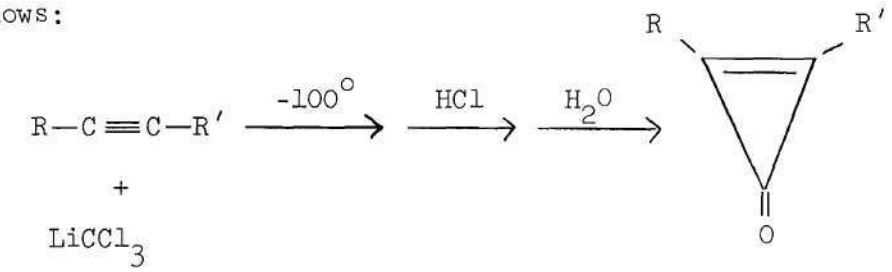
In 1965 Breslow[28] devised an even better procedure for preparing diphenylcyclopropenone involving elimination of HBr from $\alpha$ - $\alpha'$-dibromodi-



(6)

benzyl ketone. The physical and chemical properties showed that the ketone was strongly polarized, as expected for a derivative of the aromatic cyclopropenyl cation.

In 1966 Breslow[29] reacted lithium trichloromethide at -100° with various acetylenes and produced substituted cyclopropenones after hydrolysis. Using this procedure, methyl-, propyl-, dimethyl-, and dipropylcyclopropenone were prepared in moderate yields. These reactions are as follows:



(7)

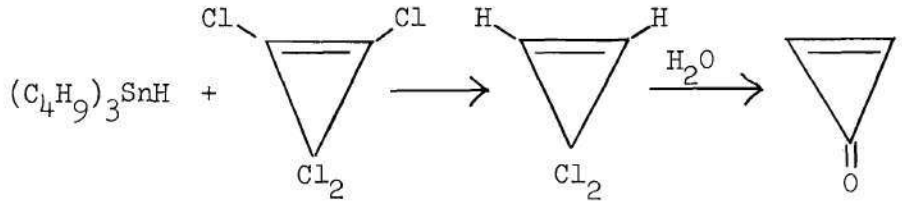
where: $R = CH_3$; $R' = H$

$R = n\text{—}C_3H_7$; $R' = H$

$R = R' = CH_3$

$R = R' = n\text{—}C_3H_7$

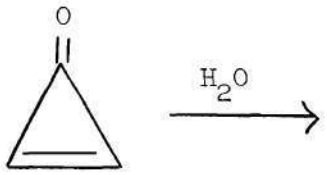
The first and only known successful synthesis of cyclopropenone was achieved in 1967 by Breslow and Ryan[5]. Tri-n-butyltin hydride was reacted with tetrachlorocyclopropene in paraffin oil at room temperature, as shown by the reaction




(8)

The volatile mixture of chlorocyclopropenes was taken up in carbon tetrachloride and hydrolyzed. Only cyclopropenone was detected using nmr and infrared analysis.

On standing, cyclopropenone slowly ($t_{\frac{1}{2}}$ at $25^{\circ}$ > 1 week) hydrolyzed to acrylic acid.




(9)

Treatment with alkali produced a dark polymer, but the compound was stable to a variety of strong mineral acids.

Although cyclopropenone is very polar, it was extracted from the water solution using methylene chloride or ethylene chloride by salting out. Infrared and nmr analysis showed that cyclopropenone was apparently present as a free ketone rather than a gem-diol, even in aqueous solution.

Attempts to isolate cyclopropenone by solvent removal, distillation, or vapor phase chromatography under a variety of conditions failed, leading

to at least partial polymerization of the compound. Since cyclopropenone had low reactivity compared with cyclopropanone, it was concluded that the cyclopropenone system has considerable conjugative properties.

This synthesis by Breslow and Ryan was chosen as a primary model for the preparation of cyclopropenone in this work.

# CHAPTER II

## APPARATUS AND PROCEDURE FOR SYNTHESIS OF CYCLOPROPENE

The method of preparing cyclopropene was essentially that of Closs and Krantz[4] with several modifications. All chemicals used were of reagent quality.

A schematic diagram of the apparatus is shown in Figure 1. The apparatus consisted of a 100 ml. three-neck flask fitted with addition funnel, nitrogen inlet tube, and a water-jacketed condenser. The flask contents were stirred by a Fisher Lab Supplies magnetic stirrer. The condenser was joined by a ball and socket coupling to a 50-ml. gas wash bubbler containing 2N sulfuric acid. This trap in turn led via a ball and socket connection to the product trap, which was immersed during operation in a dewar of liquid nitrogen. High vacuum stopcocks controlled flow to and from the product trap. The smallest possible volume of the system was desired in order to transport the product from reaction vessel to product trap in the least amount of time, thereby reducing the chance of decomposition or polymerization.

The reaction flask was heated by a water bath which was stirred by the same magnetic stirrer which provided stirring for the reaction flask. The heating element was a 300-watt wire heater controlled by a Superior Electric Company Powerstat. Closs and Krantz used a heating mantle, but it was found that the stirred water bath provided more uniform heating.

The jacketed condenser required circulating ice water for cooling

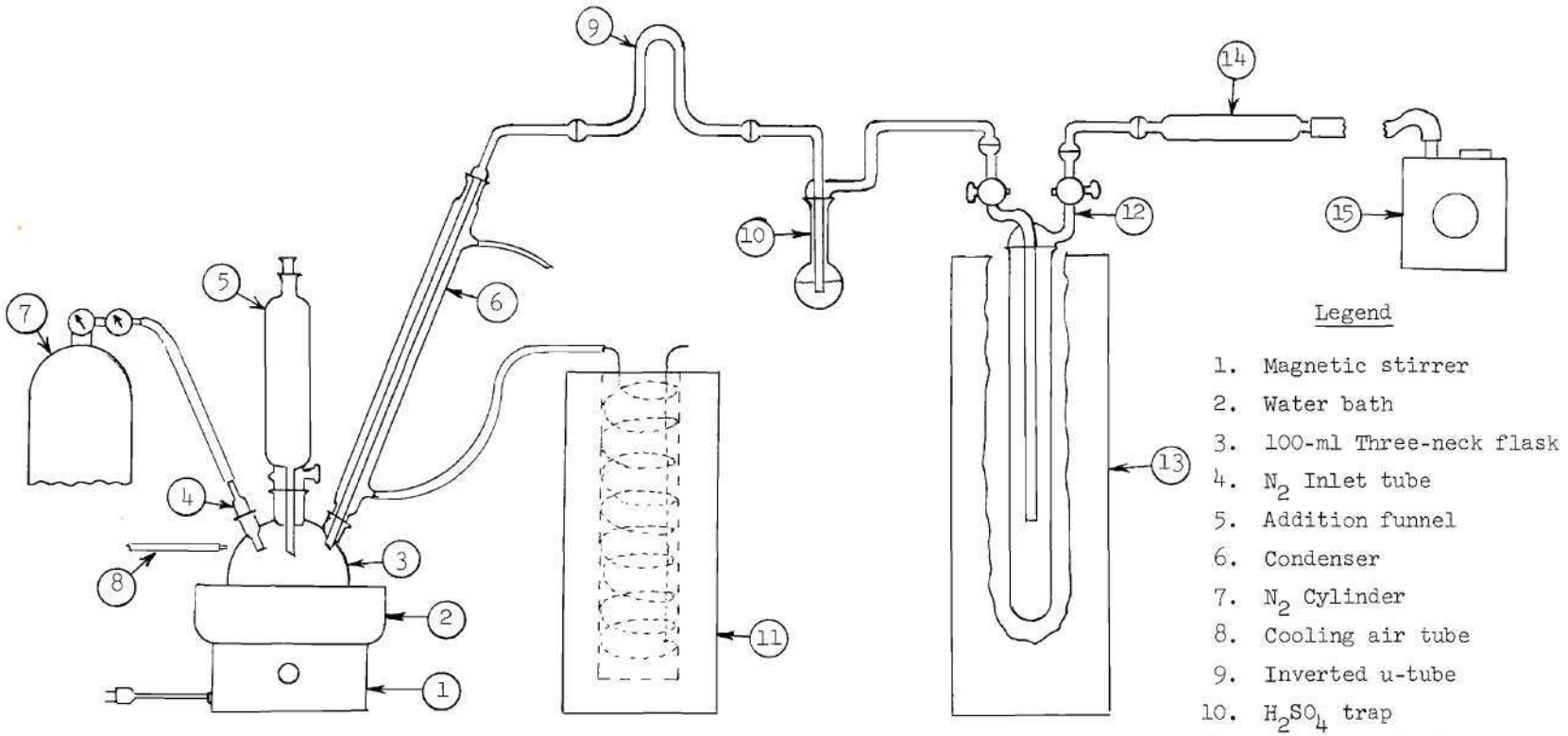


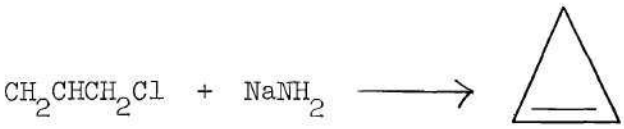

Figure 1. Apparatus for the Synthesis of Cyclopropene

the product gases. This was accomplished by passing tap water through a coiled quarter-inch copper tube immersed in a dewar containing an ice water bath. Satisfactory cooling was achieved provided the dewar was kept at least one-third full of ice.

A cylinder of dry nitrogen gas was attached to the inlet tube in the reaction flask by a piece of quarter-inch Tygon tubing. A pinch-clamp on the tubing provided fine control of the gas flow rate.

Other modifications of Closs and Krantz's equipment consisted of the addition of a drying tube to the outlet side of the product trap, and a Welch Model 1405 Duo Seal pump to the drying tube.

The formation of cyclopropene occurs according to the reaction



(10)

The reaction flask was charged with 12 gm (0.3 mole) of sodium amide plus 20 ml. of mineral (paraffin) oil. After heating the stirred suspension to 75-77°, 23 gm (0.3 mole) of allyl chloride was added dropwise to the flask. It was very important to add the allyl chloride slowly so as not to produce excessive foaming. On several occasions this foaming caused flooding of the condenser with resultant pressure buildup in the flask. This led to the nitrogen inlet tube being blown out of the flask, and the subsequent boiling out of the flask contents.

Addition of the allyl chloride (15-20 drops per minute) required from two to four hours. Heating and stirring were continued for another two hours, and during this time as the gas flow slowed down (as monitored by the gas wash bubbler), a slow rate of nitrogen was passed through the

system to sweep the product into the product trap. It was important here to keep the nitrogen flow rate very low; otherwise, unreacted allyl chloride was swept into the product trap. A flow rate of approximately one bubble per second as monitored by the gas wash bubbler was used in these preparations. The large quantities of allyl chloride which were swept into the product trap proved difficult to separate from the rather small amount of cycylopropene. Closs and Krantz used vapor phase chromatography for this purpose, but in this work cryogenic trap-to-trap distillation was successfully used. Malone[2] has reported more fully on this technique.

Difficulty was encountered in the early runs with air condensing in the product trap. This prevented the product gases from entering the trap which caused back pressure in the reaction flask and stopped the reaction. By attaching a pump to the product trap (via the drying tube), and evacuating the system before starting the reaction, most of these condensation difficulties were overcome. It was also found that by slightly pumping (5-10 inches water) on the system during the reaction, a steady flow rate of gas from flask to trap was produced. This may have had the effect of contaminating the product with allyl chloride, but was an effective method of controlling the reaction rate. Also, with the system under slight vacuum, the reaction temperature was lowered from the literature value of $80^{\circ}$ by $3\text{-}5^{\circ}$.

After several preparations of cyclopropene, it was found advantageous to insert an inverted U-tube between the condenser and gas wash bubbler. This kept acid from being drawn out of the bubbler and back into the flask, should the flask be cooled too quickly. Some cooling was necessary in the

early preparations because of the tendency of the flask contents to foam. As was mentioned previously, slow addition of the allyl chloride was essential; however, even with this precaution, foaming sometimes occurred making it necessary to cool the flask. This was most satisfactorily achieved by directing two small jets of air onto the upper part of the reaction flask. If this cooling were effected too rapidly, a vacuum would occur in the flask, drawing acid from the gas bubbler into the flask and thus ruining the reaction; thus, the extra measure of safety in using the inverted U-tube.

In the final three preparations, it was decided to use a larger reaction vessel in order to increase the yield. A three-neck, 500-ml. flask was used with the same attachments as before, and the quantities of starting materials were doubled. Not only was the yield increased, but the problem of foaming was nearly eliminated. However, product purity was adversely affected as a considerable quantity of allyl chloride was trapped with the cyclopropene, making more extensive purification necessary.

Since the normal boiling point of cyclopropene is $-36^{\circ}$, and the compound is highly reactive, product samples had to be kept at very low temperatures to prevent their polymerization or decomposition. All samples were stored in liquid nitrogen until analysis or further study.

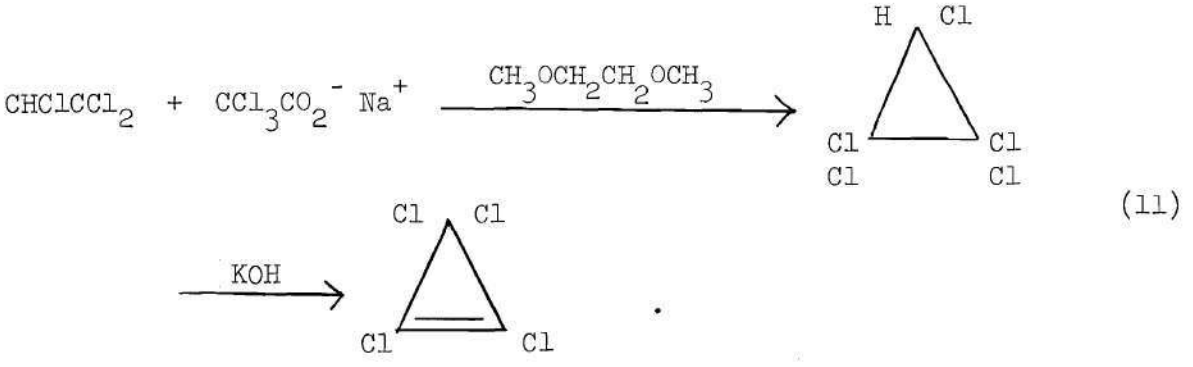
# CHAPTER III

## APPARATUS AND PROCEDURE FOR SYNTHESIS OF CYCLOPROPENONE

The preparation of cyclopropenone was carried out in three major steps: the preparation of tetrachlorocyclopropene; the preparation of tri-n-butyltin hydride; the reaction of tetrachlorocyclopropene and tri-n-butyltin hydride to form cyclopropenone. Reagent grade chemicals were used in all steps.

### Preparation of Tetrachlorocyclopropene

Tetrachlorocyclopropene was produced by the reaction of trichloroethylene with sodium trichloroacetate in dimethoxyethane as a solvent to yield pentachlorocyclopropane which was then dehydrohalogenated,




(11)

The apparatus used here was basically the same as that of Tobey and West[19] but with several modifications.

The first step in preparing tetrachlorocyclopropene was the preparation of pentachlorocyclopropane.

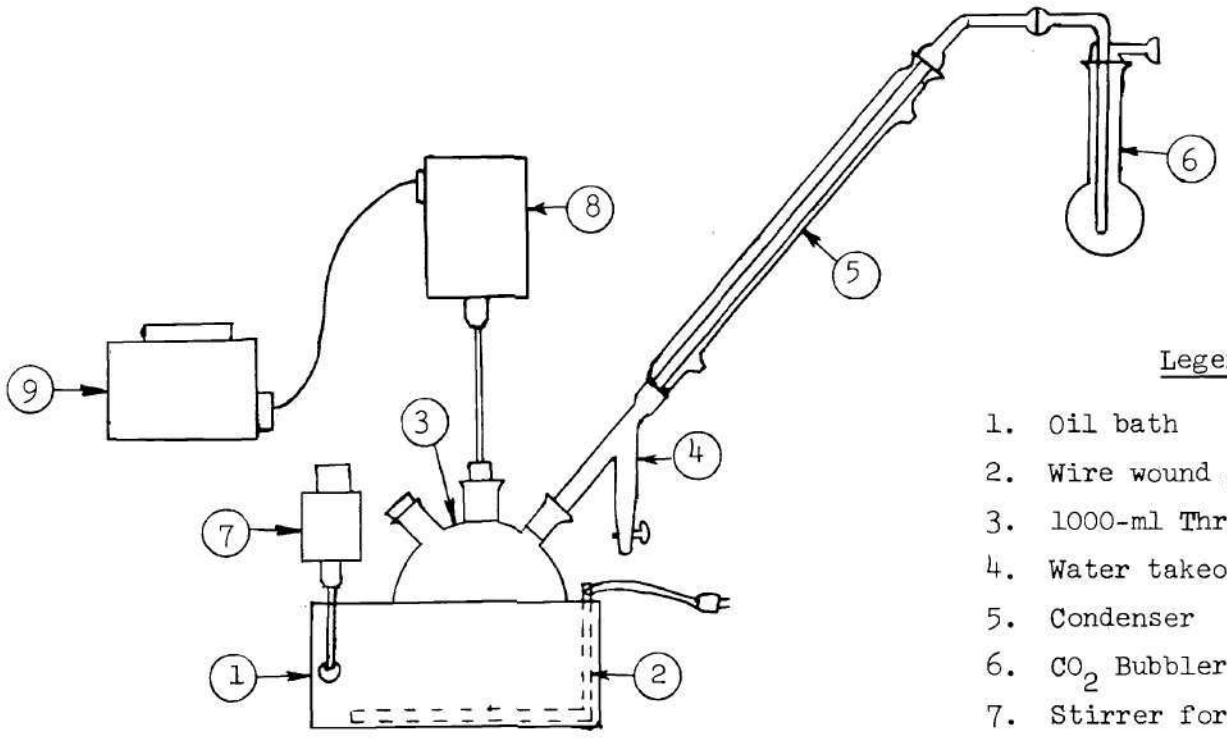
A schematic diagram of the apparatus used in this preparation is

shown in Figure 2. Five hundred ml. of trichloroethylene and 320 gm of pelletized sodium trichloroacetate were placed in a one-liter, three-neck flask fitted with a glass stirring rod and water takeoff trap leading to a reflux condenser. The condenser was vented through a 100 ml. mineral oil bubbler. The stirrer was driven by a Universal Electric Company motor whose speed was controlled by a Superior Electric Company Powerstat. Heating was by a mineral oil bath using a nichrome wire wound circular glass rod as the heating element. Energy input to the heater was controlled by a Superior Electric Company Powerstat. The bath was stirred by a glass stirring rod driven by a No. 7605 Palo Laboratory Supplies variable speed motor.

Stirring and reflux of the trichloroethylene and sodium trichloroacetate were continued for two to three hours at $80^{\circ}$ until all water had been removed (usually 8-10 ml.). To the flask was then added 150 ml. of dimethoxyethane. The suspension was refluxed at $80^{\circ}$ for 2.5 days, during which time $CO_2$ was continuously given off as monitored by a bubbler, and the reaction mass gradually darkened to a chocolate-brown color. At no time was all of the reaction material in solution. During reflux a small amount of very irritating and noxious gas evolved making use of a hood necessary.

After the reflux period, the flask was allowed to cool and its contents to settle. The brown silt settled to the bottom of the flask with about 200 ml. of a clear oil rising to the top. This upper oily layer was decanted off and the silt drenched with 100 ml. of water which provided about 50 ml. more oil.

The combined oils were first stripped under vacuum (20 mm ) to remove




Legend

1. Oil bath
2. Wire wound glass rod heater
3. 1000-ml Three-neck flask
4. Water takeoff trap
5. Condenser
6. $CO_2$ Bubbler
7. Stirrer for oil bath
8. Stirrer for reaction flask
9. Powerstat

Figure 2. Apparatus for the Preparation of Pentachlorocyclopropane

the volatile solvents, then heated slowly to 90°. The boiling point of pentachlorocyclopropane at 20 mm is 75°, but all vapor coming off from 68° to 90° was collected as product. As was expected, this product proved to contain impurities, but these were accepted in order to make sure that all pentachlorocyclopropane was collected. Figure 3 shows a diagram of the apparatus used in the distillation. This apparatus consisted of a 500-ml. distilling flask to which was attached a vacuum reflux head. A Welch Model 1405 Duo Seal pump was used to maintain the low distillation pressure. In line between the reflux head and vacuum pump, were a U-tube manometer and a 500-ml. trap immersed in liquid nitrogen. All vapors coming from the distilling flask were condensed in this trap and prevented from entering the pump. Uniform heating was provided by a mineral oil bath heated by a nichrome wire wound glass rod whose power input was controlled by a Superior Electric Company Powerstat.

Early attempts to use a reflux condenser between the flask and reflux head were unsuccessful as product vapors condensed within the condenser and very little product reached the reflux head. Thus, all the later runs were conducted with the reflux head attached directly to the distilling flask. Using this technique, approximately 50 ml. of product, a clear oil with irritating smell was collected in each run. Characterization of the pentachlorocyclopropane was established using mass and infrared spectrometry. No special precautions were taken in storing the pentachlorocyclopropane prior to its conversion to tetrachlorocyclopropene since the cyclopropane derivative is a stable liquid at room temperature.

Formation of tetrachlorocyclopropene occurs under very mild conditions, involving the removal of an HCl molecule from the pentachlorocyclo-

Legend

1. Oil bath
2. Heating element
3. Distilling flask
4. Vacuum reflux head
5. Product flask
6. Cooling bath for product flask
7. U-tube manometer
8. Pump safety trap
9. Pump safety trap dewar
10. Pump

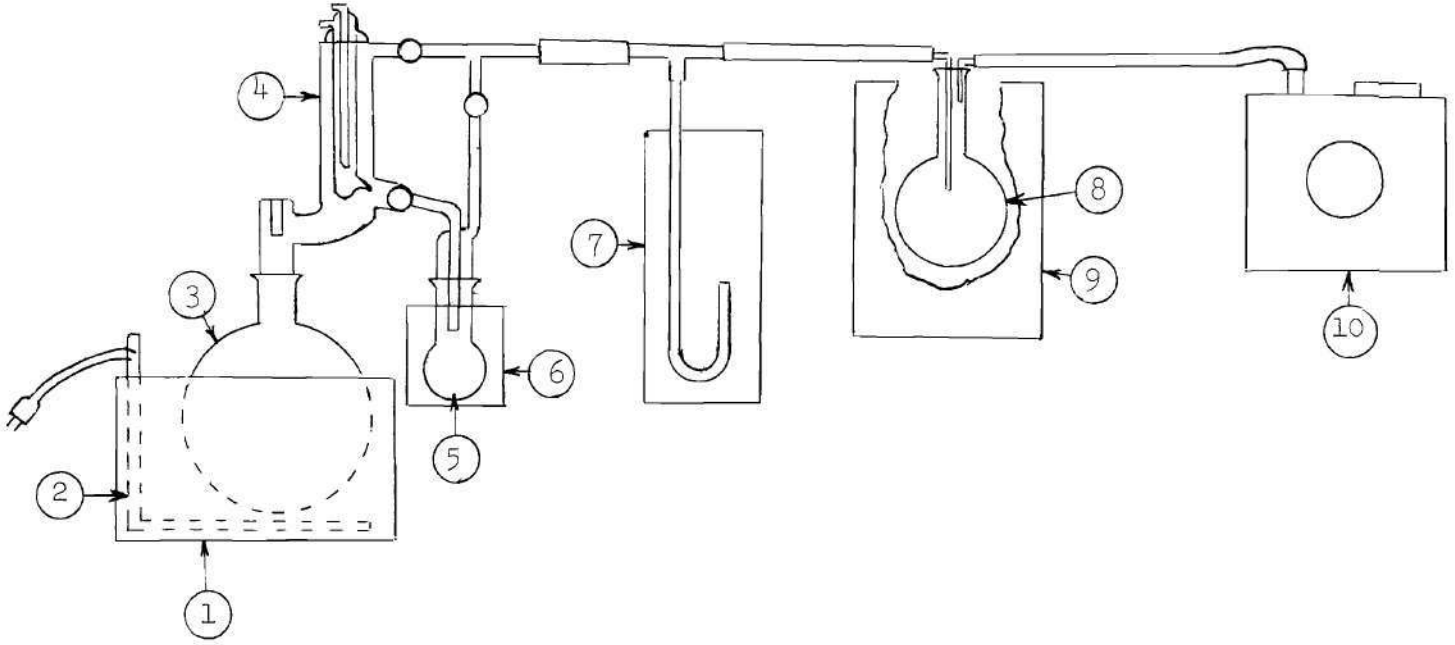



Figure 3. Apparatus for Distilling Pentachlorocyclopropane

propane molecule.

To 50 gm of pentachlorocyclopropane was added 0.6 mole KOH dissolved in 40-ml. water. The emulsion which formed was swirled for 30 minutes and occasionally cooled to make sure the reaction temperature did not exceed $100^{\circ}$.

On adding 25 ml. of cold concentrated HCl, the emulsion broke and formed two layers. The lower, oily layer was separated, dried over $CaCl_2$, and then distilled. The distillation apparatus was the same as that shown in Figure 3. All product which distilled over at up to $90^{\circ}$ at a pressure of 20 mm was collected. The boiling point of tetrachlorocyclopropene at 745 mm is $130^{\circ}$[19].

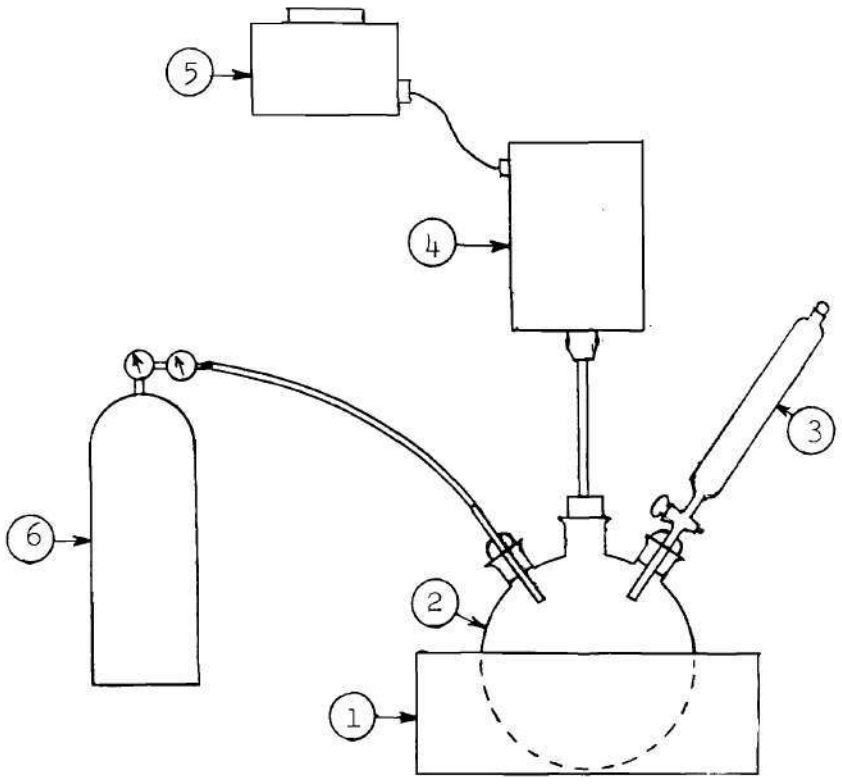
Tetrachlorocyclopropene was characterized by infrared analyses. Due to the good stability of tetrachlorocyclopropene at room temperature, no special measures were taken in storing it prior to its further use.

## Preparation of Tri-n-butyltin Hydride

At the time of this synthesis, tri-n-butyltin hydride was not commercially available and was prepared by the method of Kuivila[30]. This method involves the reduction of tri-n-butyltin chloride by lithium aluminum hydride in an ether solution. The reaction is as follows:

$$(H_3CCH_2CH_2CH_2)_3\ SnCl \xrightarrow{LiAlH_4} (H_3CCH_2CH_2CH_2)_3\ SnH \quad . \qquad (12)$$

A diagram of the apparatus used in this preparation is shown in Figure 4. To a 500-ml., three-neck flask which was cooled in an ice water bath and fitted with a dropping funnel, glass stirring rod, and nitrogen inlet tube, was placed 155 ml. of anhydrous ether. The stirring rod was




Legend

1. Ice-water bath
2. 500-ml Three-neck flask
3. Addition funnel
4. Stirrer
5. Powerstat
6. $N_2$ Cylinder

Figure 4. Apparatus for the Synthesis of Tri-n-butyltin Hydride

driven by a Universal Electric Company variable speed motor. To the ether was then added 40 gm of tri-n-butyltin chloride and 1.93 gm of lithium aluminum hydride.

The milky mixture was stirred at bath temperature for 15 minutes, then at room temperature for three hours. The mixture was then slowly hydrolyzed with 105 ml. of cold water. An ether and water layer formed. The ether (upper) layer was separated, washed with two 50-ml. portions of ice water, then dried over magnesium sulfate. Approximately 130 ml. of a clear liquid remained at this point.

The ether was distilled off at room temperature and the hydride distilled rapidly at one mm pressure using an oil bath preheated to 90°. The distillation apparatus, as shown in Figure 5, consisted of a 100-ml. distilling flask heated by the oil bath and connected by ball and socket to a 100-ml. product trap cooled in liquid nitrogen. To the product trap was connected a U-tube manometer, 500-ml. pump safety trap cooled in liquid nitrogen, and a Welch Model 1405 Duo Seal pump. About 30 ml. of product, a clear liquid, was obtained with approximately 10 ml. remaining in the still. Mass spectrometric analysis confirmed that the desired product, tri-n-butyltin hydride, had been produced. The product was sensitive to oxygen and was stored under argon in a desiccator.

## Preparation of Cyclopropenone

The apparatus for the preparation of cyclopropenone is shown in Figure 6. Three gm of tetrachlorocyclopropene in 40 ml. of mineral oil were placed in a three-neck, 100-ml. round bottom flask. This flask was fitted with a dropping funnel, nitrogen inlet tube, and was connected by

Legend

1. Oil bath
2. Heating element
3. Distilling flask
4. Product trap
5. Product trap cooling flask
6. U-tube manometer
7. Pump safety trap
8. Pump safety trap dewar
9. Pump

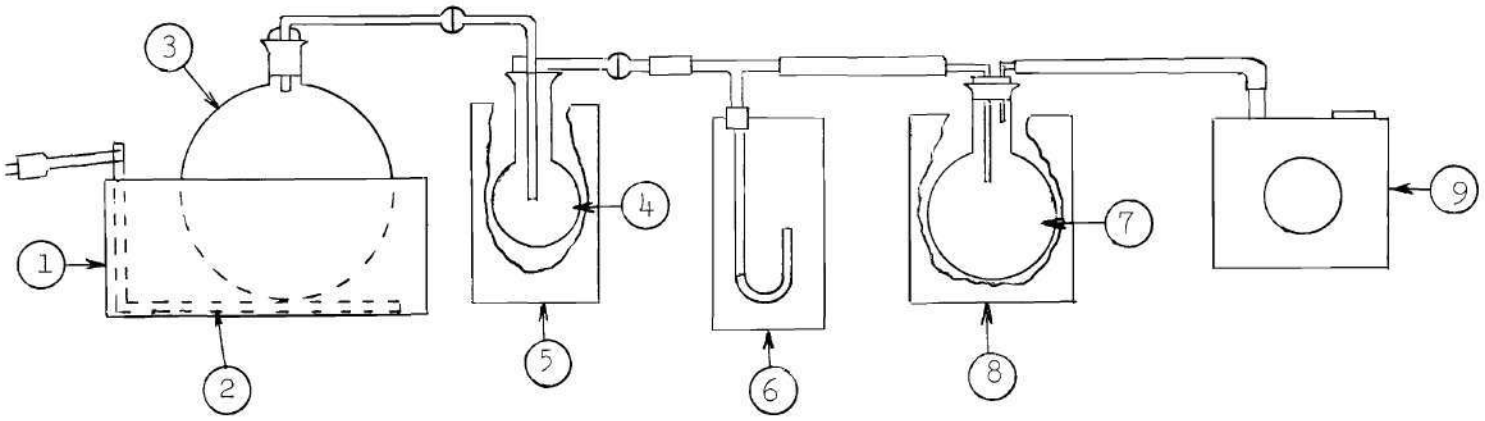



Figure 5. Apparatus for Distilling Tri-n-butyltin Hydride

Legend

1. 100-ml Three-neck flask
2. Coding water bath
3. Magnetic stirrer
4. $N_2$-Inlet tube
5. Addition funnel
6. Product trap
7. Product trap cooling flask
8. U-tube manometer
9. Pump
10. $N_2$ Cylinder

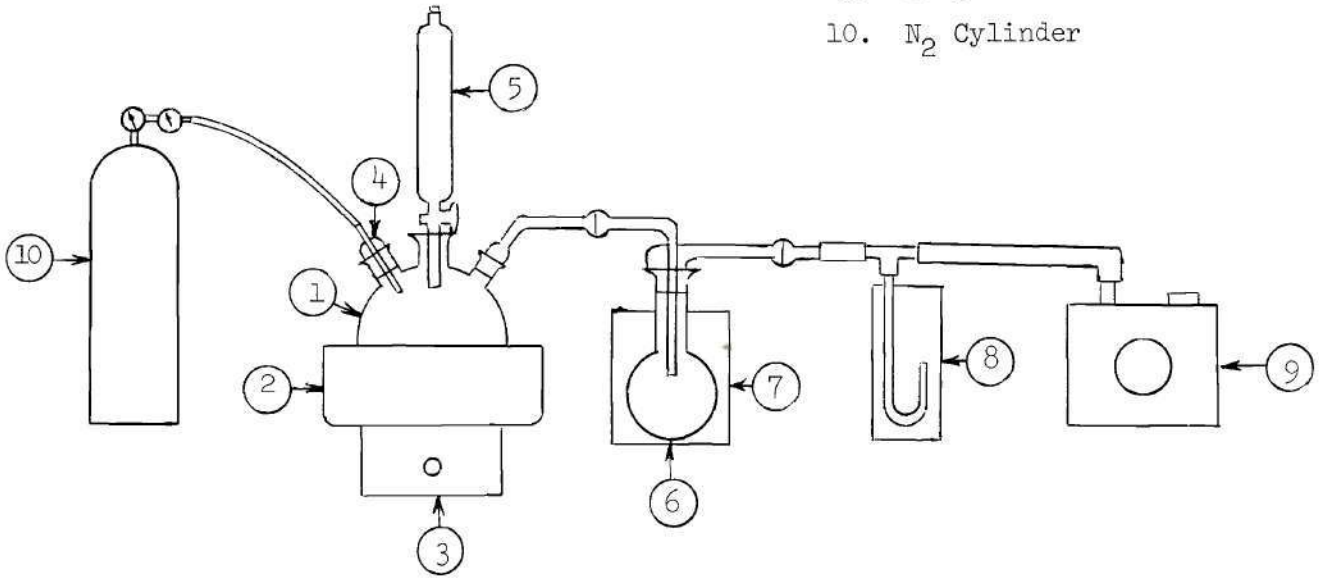



Figure 6. Apparatus for the Synthesis of Cyclopropenone

ball and socket to a 100-ml. trap cooled by an ice-acetone bath. To this product trap were connected a U-tube manometer and a Welch Model 1405 Duo Seal pump. After flushing the flask with dry nitrogen gas, 15 gm of tri-n-butyltin chloride was added dropwise. The solution was stirred by a Fisher magnetic stirrer, and during addition of the hydride the flask was cooled by an ice water bath. Stirring was continued overnight at room temperature. The flask contents were then distilled at 1 mm and room temperature into the chilled product trap. Approximately one ml. of a clear liquid was collected in the trap, and to this was added two ml. of carbon tetrachloride. Hydrolysis of the product, a mixture of dichlorocyclopropenes, could be performed when desired by adding a few drops of deuterium oxide or water to the sample. In general, the unhydrolyzed product was kept until time for analysis. Nmr analysis was used to characterize the products, a mixture of the 1,3- and 3,3-dichlorocyclopropenes.

Characterization of the product cyclopropenone was obtained from nmr analysis. Cyclopropenone was kept frozen at liquid nitrogen temperature when not being analyzed or studied.

In the final preparation of cyclopropenone, enough tetrachlorocyclopropene and tri-n-butyltin hydride was produced to yield about 30 gm of cyclopropenone. The procedures for preparing the tin hydride and tetrachlorocyclopropene were identical to those just given, only the quantities of materials used differed.

In preparing pentachlorocyclopropane, 2500 ml. of trichloroethylene was reacted with 1600 gm of sodium trichloroacetate in 750 ml. of dimethoxyethane. This produced 3400 ml. of clear liquid to be distilled. About 2600 ml. of ether was vacuum-stripped at room temperature. Distillation of

the remaining liquid yielded 160 ml. of pentachlorocyclopropane with 75 ml. of a thick, brown residue remaining in the distillation flask. Some 350 ml. of trichloroethylene and dimethoxyethane were also collected in this distillation as determined from the infrared analysis of the various cuts.

Approximately 15 ml. of incompletely converted tetrachlorocyclopropane from a previous run was added to the 160 ml. of fresh pentachlorocyclopropane, and the mixture was reacted with 15 M KOH to form tetrachlorocyclopropene. Distillation yielded 110 ml. of product tetrachlorocyclopropene. However, this product also contained some unconverted pentachlorocyclopropane and it was therefore redistilled to obtain a more pure product. The final yield of tetrachlorocyclopropene was about 90 ml.

In preparing the tin hydride, 500 gms of tin chloride was reacted with 24 gm of $LiAlH_4$ in 2310 ml. of ether. Vacuum stripping followed by distillation at $90^{\circ}$ and 1 mm pressure produced about 300 ml. of tri-n-butylin hydride.

A trial run was carried out to prepare cyclopropenone in larger quantities than in the previous trials. Ten gm of tetrachlorocyclopropene and 50 gm of tin hydride were reacted to yield 2.25 gm of the dichlorocyclopropenes. When hydrolyzed, these dichlorocyclopropenes formed from 2 to 10 ml. of cyclopropenone solution, depending on the concentration desired.

# CHAPTER IV

## RESULTS AND DISCUSSION

Cyclopropene and cyclopropenone were successfully synthesized using the methods given in Chapters I and II of this work. In the synthesis of these compounds it was necessary to prove that the desired products had been made. Also, since the synthesis of cyclopropenone required that tetrachlorocyclopropene and tri-n-butyltin hydride be prepared first, it was necessary to identify these compounds before proceeding to subsequent steps. Several techniques were used in these analyses.

### Cyclopropene

The synthesis of cyclopropene was a one-step procedure, and it was necessary only to analyze the final product for cyclopropene. Since most of the product samples were contaminated with allyl chloride, it was necessary to purify them before analysis. This was accomplished using a trap-to-trap distillation technique developed by Martin[1] and Malone[2]. It should be noted here that this trap-to-trap distillation procedure requires that the material to be distilled be warmed to room temperature for a short period of time. Since a significant portion of the cyclopropene proved on analysis to have survived this warming without decomposition, this indicates that cyclopropene is stable at room temperature, at least for short periods of time. From mass spectrometric analysis, it was clear that this distillation technique successfully removed all traces of allyl chloride from the product.

The cryogenic mass spectrometer[1] was used for sample analysis. A major peak at mass 39 in the product spectrum confirmed the presence of cyclopropene. The question might be asked at this point as to whether the peak at mass 39 might be attributed to methylacetylene instead of cyclopropene. This is not very likely since the isomerization of cyclopropene to methylacetylene occurs fairly rapidly only at temperatures greater than 400°[14], whereas the reactions in this work were conducted at less than 80° and the products were kept frozen in liquid nitrogen. The major mass peaks in the spectrum of cyclopropene are given in Table 1.

Table 1. Mass Spectrum of Cyclopropene at 70 eV Using a Bendix Model 14-107 TOF Machine

| m/e | Relative Abundance (percent) |
|---|---|
| 42 (impurity) | 4 |
| 41 (impurity) | 8 |
| 40 | 55 |
| 39 | 100 |
| 38 | 35 |
| 37 | 23 |
| 36 | 6 |
| 27 | 5 |
| 26 | 7 |
| 25 | 5 |
| 24 | 2 |
| 20 (probable doubly charged ion) | 3 |
| 19 (probable doubly charged ion) | 4 |
| 14 | 3 |

## Cyclopropenone

The first step in the synthesis of cyclopropenone was the preparation of pentachlorocyclopropane followed by its conversion to tetrachloro-

cyclopropene. Proof of the existence of these compounds was desired before proceeding further. Mass spectrometric and infrared analysis were used in order to identify these products.

Pentachlorocyclopropane, and later tetrachlorocyclopropene were subjected to analysis using one of the mass spectrometers (time-of-flight) available in this laboratory. The spectra of both of these compounds were nearly identical. In both cases, peaks occurred around mass 177-180, the mass of tetrachlorocyclopropene, along with many fragments peaks, some of which were identifiable. These spectra agreed fairly well with the spectrum of tetrachlorocyclopropene given by Tobey and West[19]. The difficulty in interpretation results from the fact that pentachlorocyclopropane does not have a parent ion. The heaviest fragment ion corresponds to the parent ion less one chlorine atom. On the other hand, tetrachlorocyclopropene exhibits a small parent ion, but the fragment ion of largest intensity is again one chlorine mass less than the parent. Interpretations are further complicated by the obvious overlapping of the mass spectrometric structure at every mass number. Table 2 shows the mass spectrum of pentachlorocyclopropane.

The infrared spectra of pentachlorocyclopropane and tetrachlorocyclopropene were also available[19] for comparison, and hence samples from these preparations were analyzed on a Perkin-Elmer Model 221 Spectrophotometer. All samples were dissolved in carbon tetrachloride or carbon disulfide and NaCl plates were used. Major peaks at 945, 890, and 768 $cm^{-1}$ were obtained for pentachlorocyclopropane, while peaks at 1810, 1150, 1055, and 753 $cm^{-1}$ were obtained for tetrachlorocyclopropene, agreeing almost exactly with those given by Tobey and West[19]. These spectra are shown in Figures 7, 8, and 9. In addition to the product sample, samples of pure trichloroethylene

Table 2. Mass Spectra of Pentachlorocyclopropane at 70 eV Using a Varian M-66 Spectrometer

| m/e | Relative Abundance (percent) |
|---|---|
| 216 (parent) | none |
| 181 | 27 |
| 179 | 100 |
| 177 | 32 |
| 145 | 2 |
| 143 | 11 |
| 141 | 13 |
| 109 | 4 |
| 107 | 6 |
| 83 | 6 |
| 82 | 6 |
| 72 | 4 |
| 47 | 3 |
| 45 | 4 |
| 37 | 1 |
| 36 | 1 |
| 35 | 1 |

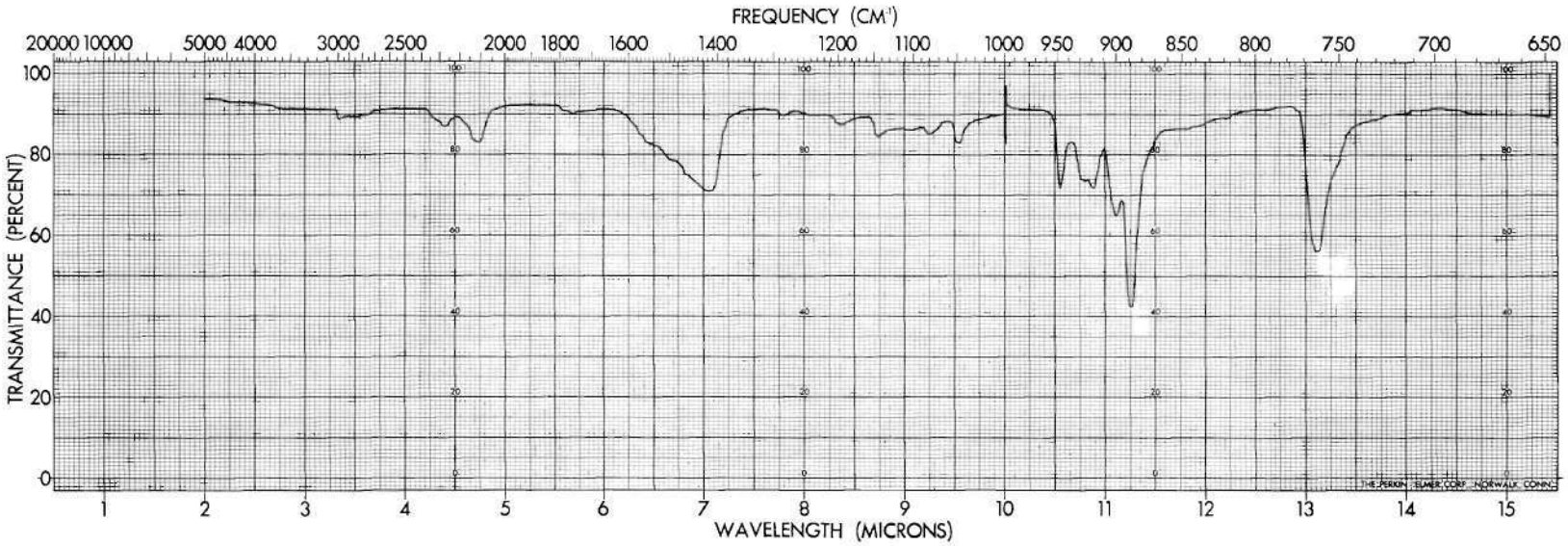



Figure 7. Infrared Spectrum of Pentachlorocyclopropane in $CS_2$

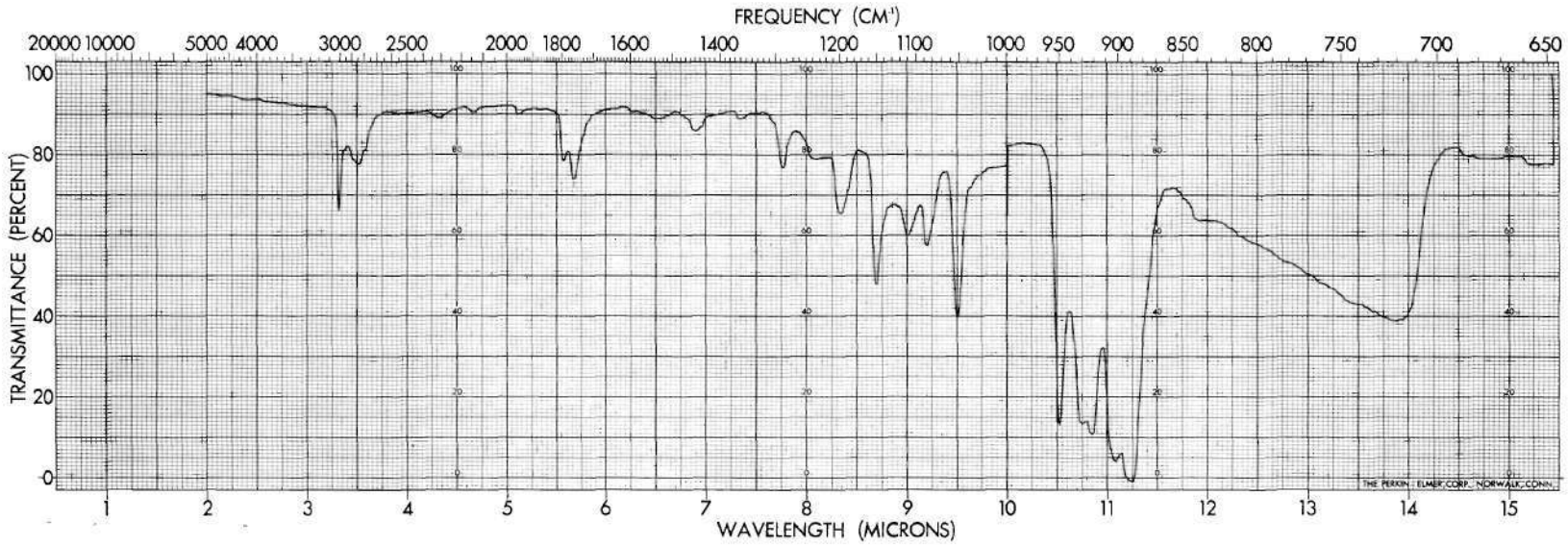



Figure 8. Infrared Spectrum of Pentachlorocyclopropane in $CCL_4$

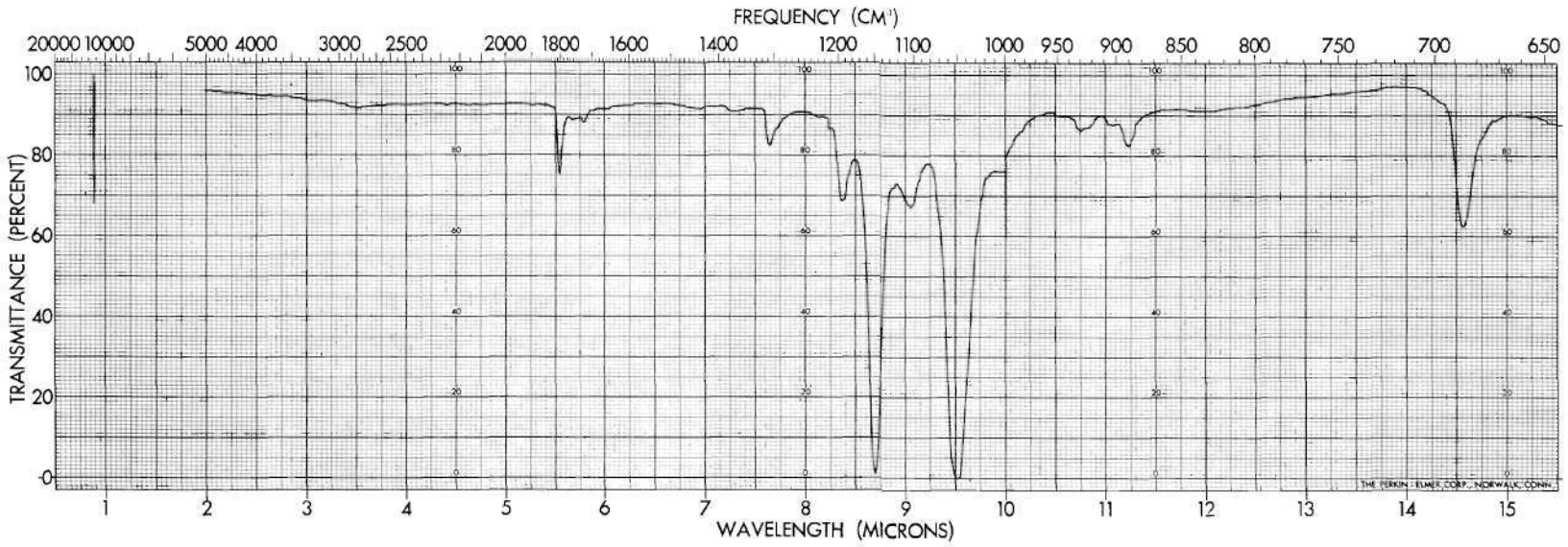



Figure 9. Infrared Spectrum of Tetrachlorocyclopropene in $CCL_4$

and 1,2-dimethoxyethane, the solvents used in preparing tetrachlorocyclopropene were also analyzed. This enabled identification of all of the structure of the infrared spectrum with the exception of two peaks, which were attributed to impurities.

Identification of tri-n-butyltin hydride was accomplished mass spectrometrically. The spectra showed structure at 121, 177, 235, and 291, which were readily attributed to tri-n-butyltin hydride (see Figure 10). Additional major structure at 199, 257, 269, and 313 were tentatively attributed to a tin-magnesium complex. The magnesium complex may have come from the $MgSO_4$ used in drying the tin hydride before distillation, but its presence did not seem to affect the purity or yield of cyclopropenone when used to prepare that product. Figure 10 shows the complete mass spectrum of the final product tri-n-butyltin hydride and its associated impurities.

Proof of the presence of cyclopropenone in the final step of synthesis was achieved using nmr analysis. Results that were obtained using a Varian Model A-60 nmr machine compared almost exactly with those reported by Breslow and Ryan[5].

A sample, assumed to contain 1,3- and 3,3-dichlorocyclopropene was taken up in carbon tetrachloride and analyzed. Both internal and external standards (tetramethylisilane) were used. Peaks were observed at $\delta 8.0$, $\delta 7.2$ and $\delta 4.5$. The peaks at $\delta 7.2$ and $\delta 4.5$ were attributed to the 1,3-dichlorocyclopropene while that at $\delta 8.0$ was attributed to the 3,3-dichlorocyclopropene. These values agreed exactly with those reported by Breslow and Ryan. The mass spectrum of the mixed 1,3- and 3,3-dichlorides was also observed, and the principle peaks appear in Table 3.

Next, several drops of deuterium oxide were added to the mixed

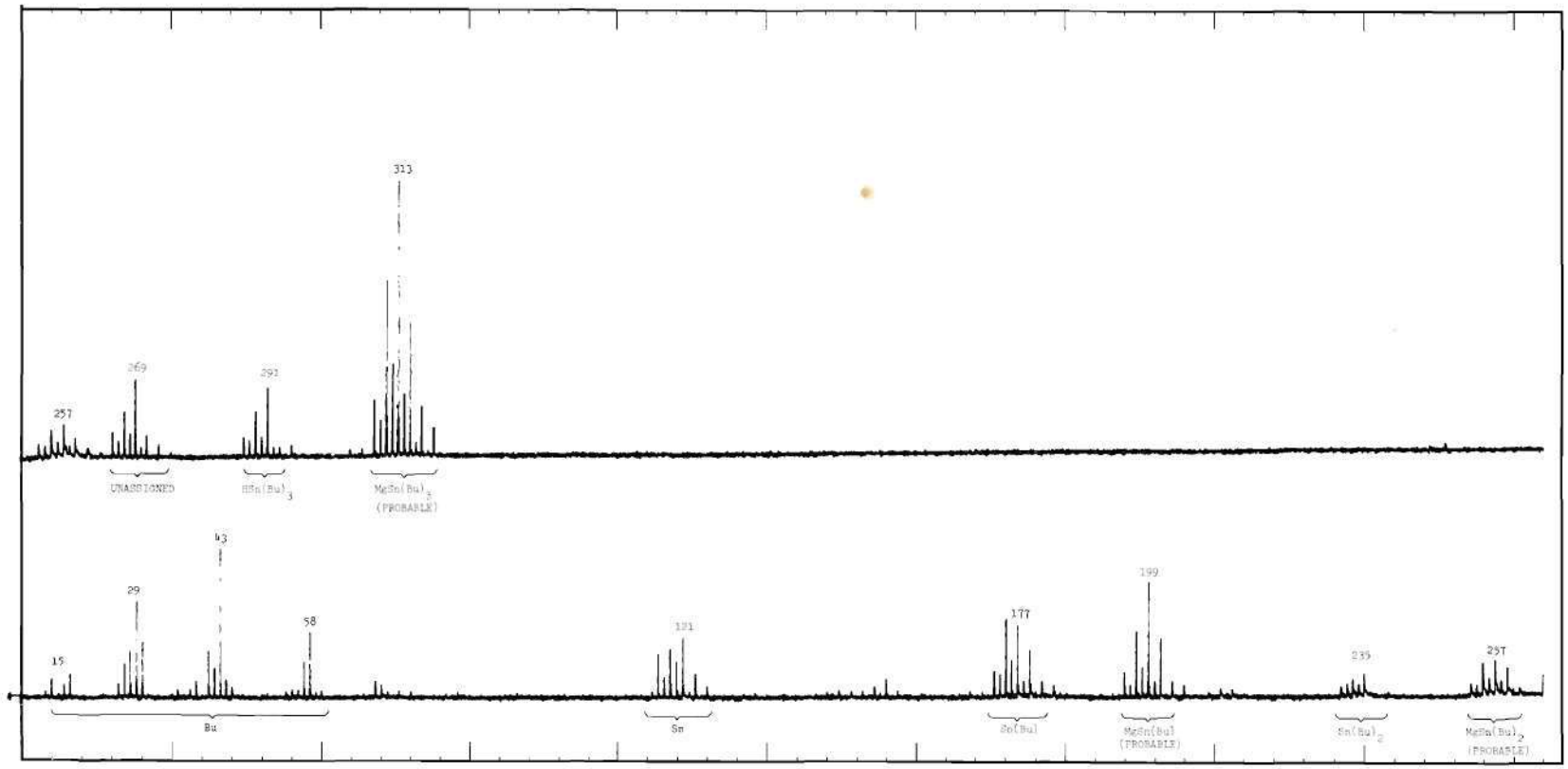



Figure 10. Mass Spectrum of Tri-n-butyltin Hydride Observed at 70 eV Using a Varian M-66 Spectrometer

Table 3. Mass Spectrum of Dichlorocyclopropene Mixture at 70 eV Using a Bendix Model 14-107 TOF Machine

| m/e | Relative Abundance (percent) |
|---|---|
| 110 | 2 |
| 108 | 2 |
| 75 | 40 |
| 73 | 100 |
| 37 | 40 |

dichlorides still contained in an nmr sample tube, and then the contents were shaken well. The upper, aqueous layer was removed and placed in a second nmr sample tube containing water. The first tube, containing the carbon tetrachloride layer was again analyzed and this time no peaks were observable at $\delta 8.0$, $\delta 7.2$, or $\delta 4.5$, indicating that the dichlorocyclopropenes had been removed. Analysis of the second tube containing the water layer showed a very strong, single peak at $\delta 9.1$. This agreed almost exactly with Breslow and Ryan's value of $\delta 9.0$ for cyclopropenone.

# CHAPTER V

## CONCLUSIONS AND RECOMMENDATIONS

As a result of the work done in this study, the following conclusions can be made.

1. Cyclopropene was successfully produced by the reaction of allyl chloride and sodium amide. Purification and characterization were achieved using the cryogenic mass spectrometer as developed in this laboratory. Sufficient quantities of cyclopropene were prepared and stored to allow studies of the moleculer energetics and stability of this strained ring hydrocarbon.

2. Cyclopropenone was successfully synthesized by the reaction of tetrachlorocyclopropene and tri-n-butyltin hydride. Because both tetrachlorocyclopropene and tri-n-butyltin hydride are not commercially available, they had to be prepared from readily available materials. Characterization of these intermediate products was accomplished using mass spectrometric and infrared analysis. Cyclopropenone was characterized by nmr analysis.

Enough tetrachlorocyclopropene (75 percent purity) is presently on hand to make 13 gms of the dichlorocyclopropene mixture (purity unknown) assuming our best yield of about 40 percent. The tri-n-butyltin hydride appears to be undergoing some reaction during storage as a white precipitate is forming. Its purity is questionable and more tin hydride should be obtained before subsequent dehalogenation of the tetrachlorocyclopropene is

attempted.

3. Synthesis procedures for cyclopropene and cyclopropenone were obtained from the literature and were modified or changed to suit the conditions of this laboratory and the available equipment. This work should serve as a manual for future preparations of cyclopropene and cyclopropenone in this laboratory.

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* Abbreviations herein follow the form used by Chemical Abstracts (1965).

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